

Analytical Chemistry Laboratory

Highlights for October through December 1999

The Analytical Chemistry Laboratory (ACL) provides analytical chemistry services and technical support for a variety of programs at Argonne National Laboratory (ANL), works collaboratively with programs, and conducts independent research in analytical chemistry. For more information on any of these highlights, call one of the individuals listed with the highlight or the ACL Office at (630) 252-4473.

Information about the ACL is available through its World Wide Web home page at <http://www.cmt.anl.gov/acl/acl.htm>. Topics available from this home page include:

- ✓ Advice on how to submit samples
- ✓ Major technical specialties of the ACL staff
- ✓ ACL Quarterly Highlights since October 1994
- ✓ ACL Annual Reports for FY 1996, 1997, and 1998
- ✓ List of all published ANL/ACL technical reports

David W. Green, Manager

New Alpha Analyst / Integrated Alpha Spectrometer (F. Markun and L. L. Smith)

The ACL recently acquired a new Canberra 24-chamber alpha spectrometry system called the Alpha Analyst. It is computer controlled to simplify analysis and record keeping. Built-in features include the ability to monitor the performance of both the instrument and the sample chemistry. The instrument offers simplified setup and calibration, ease of sample processing, improved alpha spectrum analysis, and enhanced quality assurance.

The instrument also came equipped with a built-in recoil suppressor and a "Clean Vent" option, which allows the system to be flushed with radon- and moisture-free air. Both features help to prevent the detectors from becoming contaminated so as to maintain consistently low backgrounds in the spectrometer chambers and extend the useful operating life of alpha detectors.

With the acquisition of the new Alpha Analyst we increased our counting capability by 50%, from 16 detectors to 24 detectors. This increased capacity will enable us to process many more samples in a shorter time period with better-documented quality assurance.

Method for Determining Halide Impurities in Refractory Materials (A. M. Essling, F. P. Smith, and D. G. Graczyk)

Measurement of small amounts of halides contained in refractory materials is difficult because methods generally used for decomposing the refractory can volatilize the sought-for elements or interfere with their determination. One approach that has been considered in the ACL is the use of a potassium hydroxide fusion to decompose siliceous or aluminosilicate refractories, followed by ion chromatographic analysis of the basic solution obtained by treating the fusate with water. Although sometimes successful, this approach often failed when the aluminum content of the refractory was high so that fluoride was complexed, or the halide content was low. Recently, the method was modified to overcome these problems and tested for analysis of lithium aluminate. In it, a 0.5-g sample is fused with 4 g of KOH in a zirconium crucible. The fusate is carefully neutralized and then dissolved with sulfuric acid, which completely solubilizes the sample. Then, more sulfuric acid is added, and the halides are steam distilled from the mixture. The distillate is analyzed by ion chromatography. Preliminary tests of the method have shown 75% or better recovery of fluoride, chloride, and bromide at levels equivalent to 0.03 wt.% in the solid sample. Iodide was absent from the distillate, possibly as a result of oxidation to other iodine species such as I₂ or iodate. This new approach is being applied in determining F, Cl, and Br in lithium aluminate ceramics. It promises to be useful for analysis of glasses, zeolites, waste form samples, and other materials.

High-Precision Assay of Lithium and Aluminum (D. G. Graczyk, D. R. Huff, S. J. Lopykinski, and A. M. Essling)

The ACL is continuing investigation of alternative methods for chemical analysis of lithium aluminate ceramic materials. The goal of this work is to determine whether certain established and qualified, but inefficient, methods can be replaced with modern alternatives that would be more attractive for production-lot analyses in private sector laboratories.

The ACL is investigating a novel methodology developed at the National Institute of Science and Technology (NIST) for making exceptionally precise measurements using inductively coupled plasma-atomic

emission spectrometry. The approach has been used by NIST to measure the lithium and aluminum content of lithium aluminate ceramics and promises considerable advantages compared to the classical methods currently used (isotope dilution for determining lithium and gravimetric analysis for aluminum).

Early work in the ACL showed that the method provided excellent precision (0.1% relative standard deviation) with our grating-polychromator instrument when standard solutions were analyzed. Later work with standards that contained lithium and aluminum in differing proportions and measurements on lithium aluminate materials of known composition, however, indicated that the data may be biased by matrix effects or spectral differences between the analysis lines used for key elements (lithium, aluminum, and manganese, used as an internal standard). A systematic investigation of these effects as they relate to plasma conditions was completed recently and showed that problems with aluminum could be overcome by optimizing conditions, particularly nebulizer flow. Although good performance with lithium could also be achieved when the isotopic compositions of samples and standards were the same, we found that errors arose when isotopically different materials were processed. This shortcoming cannot be overcome with a grating-polychromator/photomultiplier instrument like ours. We have concluded that isotopically different lithium must be determined with an array-detector system (as used by NIST), which allows integration of the entire lithium peak profile. By sending samples to a vendor of such instruments for analysis, we demonstrated that our version of the NIST procedure works on that equipment. We are pursuing procurement of the instrument for this application.

Performance Demonstration Program for Waste Isolation Pilot Plant (A. S. Boparai, D. V. Applegate, and M. J. Kalensky)

The Waste Isolation Pilot Plant (WIPP) is a DOE installation consisting of large, interconnecting cavities hollowed out of a salt vein approximately 665 m underground near Carlsbad, NM. This facility is designed for safe disposal of radioactive transuranic waste left from the production of nuclear weapons. Before being shipped to the site, wastes must be characterized according to the Waste Analysis Plan to identify the presence of any hazardous materials in addition to radioactivity. Among other characterizations of waste destined for WIPP, the headspace gas must be analyzed for a set of target volatile organic compounds, hydrogen, and methane, and the semisolid waste sludge

must be analyzed for metals, volatile organic compounds, and semivolatile organic compounds. The National Transuranics Program Office of the Carlsbad Area Office (CAO) of DOE has established a performance demonstration program (PDP) for laboratories that will participate in the analysis of headspace gas and solidified waste (sludge) to be shipped to the WIPP site. The ACL was selected as the laboratory to prepare, analyze, and distribute samples for the headspace PDP. The ACL also prepares blank Type I sludge to be used as the interfering matrix for determination of metals.

During the last quarter, 2 kg each of cemented and uncemented samples of simulated blank Type I sludge were prepared and sent to a vendor for spiking and distribution to participating laboratories. The next set of samples for Headspace Gas PDP will be sent during early February to nine participating laboratories. Each laboratory will receive four SUMMA canisters (6 L) containing test analytes and a canister to serve as a blank sample. Sufficient 6-L canisters needed for the next PDP cycle have been cleaned and are being certified for cleanliness.

Technical Support for National Analytical Management Program (W. E. Streets)

Over the course of several years, the National Analytical Management Program (NAMP) and its predecessors within the DOE's Office of Environmental Management (EM) have developed four centralized information databases. These databases include the DOE Procedures Database, which was used to produce a World Wide Web document, *DOE Methods for Evaluating Environmental and Waste Management Samples (DOE Methods Compendium)*; the National Sample Tracking System (NSTS); the Directory of EM Sampling and Analysis Resources (DEMSAR); and the Integrated Performance Evaluation Program (IPEP).

The IPEP was developed by ANL and has continued to accumulate data from several analytical performance evaluation programs. In FY 1999, NAMP transferred the other three databases to ANL. We are in the process of consolidating the common administrative information into a single database to provide a single input source for gathering information required for IPEP reports and other projects within NAMP. Much of the work with databases was done with the assistance of the CMT Computer Applications, Network, and Security Group (J. Copple, A. Scandora, J. Kulaga, and R. Krol).

We are continuing to participate on the interagency Methods and Data Comparability Board (MDCB), founded by the National Water Quality Council to normalize assessment of water data being collected by various organizations and agencies. We are advising on design and assessing the development of the National Environmental Methods Index (NEMI), a web-based database.

In this quarter we have collected additional results data from the national performance evaluation programs conducted by DOE and EPA and loaded these into the IPEP database.

Publications

"Team Celebration," D. W. Green, Managing the Modern Laboratory, 4(2), 19A (1999).

"Fluid-Based System for Radon Mitigation," K. C. Gross and F. Markun, Argonne National Laboratory, published in the Proceedings of the 1999 International Radon Symposium, sponsored by the American Association of Radon Scientists and Technologists, Las Vegas, NV, November 9-12, 1999.

"Effect of Spectral Resolution on Pattern Recognition Analysis Using Passive Fourier Transform Infrared Sensor Data," A. S. Bangalore, J. C. Demirgian, and A. S. Boparai, Argonne National Laboratory, Argonne, IL, and G. W. Small, Clippinger Laboratories, Athens, OH, Applied Spectroscopy, Vol. 53, No. 11, November 1999.

Talks Presented

"Special Analytical Services for U.S. EPA Region V Emergency Response Branch: Chemical Agent Analysis," J. F. Schneider, Argonne National Laboratory, presented at the U.S. EPA Region 5 NBC Exercise, Cincinnati, OH, October 19-21, 1999.

"Status of Development of NAMP Informational Database Systems," W. E. Streets and A. E. Scandora, Argonne National Laboratory; J. S. Morton and S. Woolf, U.S. DOE National Analytical Management Program, presented at NAMP SMO Workshop '99, Las Vegas, NV, October 28-29, 1999.

"Fluid-Based System for Radon Mitigation," K. C. Gross and F. Markun, Argonne National Laboratory, presented at the 1999 International Radon Symposium, sponsored by the American Association of Radon Scientists and Technologists, Las Vegas, NV, November 9-12, 1999.